Argonne National Laboratory

THE EBR-II SKULL RECLAMATION PROCESS
Part IV. Pilot-plant Development

by

Irvin O. Winsch, R. Dean Pierce,
David E. Grosvenor, Leslie Burris, Jr.,
Thomas F. Cannon, Paul J. Mack,
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Chemical Engineering Division

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ABSTRACT

A pyrochemical process has been developed for the recovery of enriched uranium from crucible skulls that result from the Experimental Breeder Reactor II (EBR-II) melt-refining process. Melt refining has been used in the EBR-II Fuel Cycle Facility to recover uranium from spent fuel discharged from the reactor. The complementary process for reclaiming uranium from crucible skulls, the skull-reclamation process, involves: (1) oxidation of the skulls to liberate them from the crucible as a free-flowing powder; (2) addition of the powder to a halide salt, and extraction of 75-95% of the nobler fission-product elements from the oxide with liquid zinc at 800°C; (3) reduction of the uranium oxide to uranium metal by contacting the salt with a Mg-20 at. % Zn alloy at 800°C; (4) removal of 95% or more of the remaining fission products by transferring away the molten salt and the metal alloy in which the metallic uranium is insoluble; (5) dissolution of the uranium in a Zn-30 at. % Mg alloy; and (6) recovery of the uranium product by retorting and melting.

The skull-reclamation process was developed and tested on both a pilot and a prototype plant scale in the Chemical Engineering Division at Argonne National Laboratory. However, a change in the EBR-II reactor status from an experimental to a test reactor precluded installation of skull-reclamation process equipment in the EBR-II Fuel Cycle Facility.

I. INTRODUCTION

The concept of on-site recovery and recycle of discharged reactor fuel has been established in Argonne's Experimental Breeder Reactor II (EBR-II) complex. Spent reactor fuel was processed and new fuel refabricated in the EBR-II Fuel Cycle Facility[1] by remote pyrochemical methods. Figure 1 is a simplified fuel-cycle flowsheet.
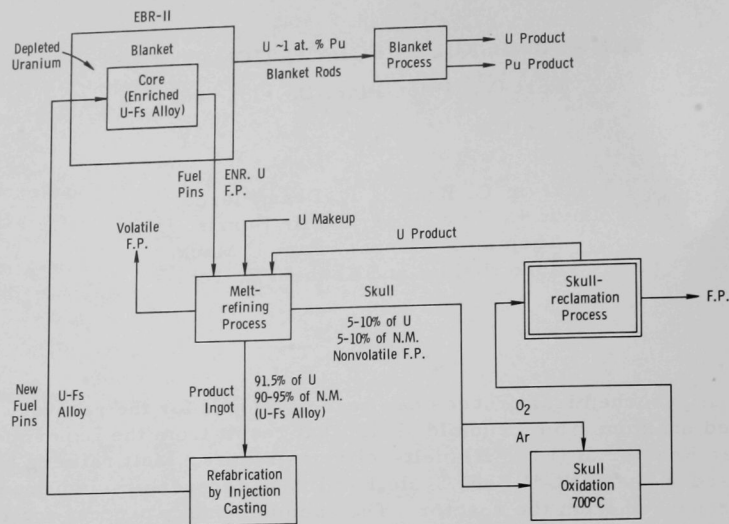
F.P. = fission products; N.M. = nobler metals; Fs = fissium.

Fig. 1. Simplified Flowsheet for EBR-II Fuel Processing

Although the EBR-II reactor may ultimately employ plutonium alloys, an enriched uranium alloy is now used as the fuel in the core loading. The core is an assembly of 0.144-in.-diam pins which are clad with stainless steel and thermally bonded with sodium. A process known as melt-refining was developed[2,3] and has been used to recover uranium from EBR-II fuel in the Fuel Cycle Facility.[4] A closed fuel cycle demonstrating remote melt refining and refabrication of fuel was operated successfully for four years with EBR-II fuel. However, because of the small scale of operation, continued operation was not justifiable economically, and processing of EBR-II fuel by pyrometallurgical methods in the Fuel Cycle Facility was discontinued early in 1969.

In the melt-refining process, the fuel pins are declad mechanically, chopped to convenient lengths, and charged along with makeup uranium to a lime-stabilized zirconia crucible. The charge is melted, heated to 1400°C, held at this temperature for about 3 hr, and then poured into a mold to form an ingot. This treatment removes about two-thirds of the fission products by volatilization of some fission elements and by selective oxidation of others through interaction with the zirconia crucible. The nobler fission products, such as molybdenum, ruthenium, and zirconium, are not removed by melt refining. The recycled fuel is an alloy of uranium and "fissium."* To avoid an alloy of changing composition, inactive nobler

*Fissium is a name given to a variable mixture of fission-product elements (atomic numbers 40 to 46) which, when alloyed with uranium, impart to the alloy desirable metallurgical properties and radiation stability.

metals are alloyed with the initial fuel in their approximate equilibrium concentrations, based on an auxiliary removal of about 7% of the nobler metals during each cycle for 2% burnup fuel. Experience has shown that the presence of these metals enhances the irradiation stability of uranium.

The product ingot is used to refabricate new fuel pins by injection casting. The fuel pins are inserted into stainless steel cans, bonded with sodium, welded, and assembled into new fuel elements for recharging to the EBR-II reactor. In the melt-refining process, inorganic radiation-stable materials are used that permit processing of short-cooled, high-burnup fuels. The rapid recycle of the fuel minimizes fuel inventories outside the reactor. Another advantage of the process is the compact equipment used.

When the product ingot is poured in the melt-refining process, about 7% of the uranium remains in the crucible as a skull, which consists of a mixture of dross and unpoured metal. In addition to uranium, the skull contains about 7% of the original nobler-metal elements and nearly all the more electropositive fission-product metals: barium, strontium, yttrium, and the rare earths.

The skull-reclamation process, a liquid-metal process for process-ing skulls,[5] was developed to fulfill three objectives: (1) recovery of the uranium, (2) removal of the electropositive fission products that are con-centrated in the skull, and (3) removal of noble- and refractory-metal fis-sion products that are not removed in the melt-refining process. Since about 93% of the fuel material is recovered in the melt-refining process, a recovery of about 95% of the fuel in the melt-refining skull will result in an overall fuel recovery of 99.6%. Decontamination requirements are mod-est, since neutron poisoning is minimal in a fast reactor and all fuel refab-rication is done remotely behind heavy shielding. It is only necessary to remove sufficient fission products to avoid excessive dilution of the fuel. Fission-product removals of 60-90% are adequate for this reactor.

A pyrochemical blanket process (as indicated in Fig. 1) was also developed. The basic equipment and operations used in the blanket process are similar to those employed in the skull-reclamation process.

II. PROCESS AND EQUIPMENT DEVELOPMENT

A total of 36 skull-reclamation runs were made in the "pilot plant" for the development of the skull-reclamation process flowsheet, equipment, and techniques. During this period, three changes were made in the process flowsheet to simplify the operations and to reduce the overall run time from 32 hr to about 11 hr.

A. Process Steps

The primary steps developed in the process flowsheets are described briefly as follows:

1. Skull Oxidation

The skull in the melt-refining crucible is burned at a controlled rate in an O_2-Ar atmosphere at 700°C.[6] This treatment converts the skull into a free-flowing oxide powder, which is poured from the crucible and is the charge to the noble-metal extraction step of the process. The oxidation step was performed along with melt refining in the Fuel Cycle Facility.[7]

2. Noble-metal Extraction

The finely divided, oxidized skull is suspended in a molten salt and contacted with zinc in a tungsten crucible. At least 50% of the relatively nobler-metal fission products are separated from the uranium by selective reduction with zinc. The reduced nobler metals, which include molybdenum, technetium, ruthenium, rhodium, palladium, silver, indium, and antimony, are extracted into the zinc, which is then removed and discarded. In the initial flowsheet, the waste-zinc phase was separated from the salt phase by cooling the crucible contents to solidify the salt. The liquid-zinc phase was then pressure-siphoned from below the salt phase to a waste receiver.

It is not essential that the reduced fission products dissolve in the zinc phase. Some of these elements have very low solubilities, and it would be unrealistic to use sufficient zinc to dissolve them completely. Mild agitation of the zinc phase during the transfer is sufficient to maintain in suspension those elements whose solubility is exceeded.

3. Reduction

The reduction of UO_2 by a liquid Mg-Zn alloy can be represented by the following overall equation:

$$UO_2 \text{ (salt)} + 2Mg(Zn) \xrightarrow{800°C} 2MgO \text{ (salt)} + U(Zn\text{-}Mg) + U\downarrow.$$
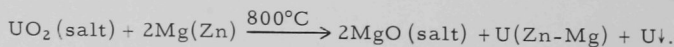
The uranium oxide, which is dispersed in the salt phase ($MgCl_2$-$CaCl_2$-CaF_2) as a solid, is reduced by the magnesium in the metal phase, and the MgO by-product collects in the salt. Slight agitation (~100 rpm) is used to suspend the insoluble MgO in the salt phase during the waste transfer. In early flowsheets, the reduction alloy was Zn-12 at. % Mg, in which the uranium was soluble; the composition of the alloy after reduction was Zn-9 at. % Mg-1 at. % U. In the final flowsheet, the UO_2 is reduced at 800°C with a Mg-20 at. % Zn alloy; the use of this alloy results in the precipitation of uranium from solution, since its solubility is only about 0.022 at. % at 800°C.

The experimental work of Knighton and Steunenberg[8] showed that molten halide salts offer advantages in the reduction of uranium oxides by molten metals. The salt promotes more complete reductions and scavenges the MgO by-product of the reaction away from the product in the metal phase.

The Mg-Zn alloy and the salt containing the rare earths, barium, strontium, and zirconium are pressure-siphoned from the crucible and treated as waste.

4. Intermetallic Compound Precipitation

With the Zn-12 at. % Mg alloy used in earlier runs, the dissolved uranium was precipitated as a zinc intermetallic compound (U_2Zn_{23}) by cooling from 800 to 525°C. This step provided zirconium removal in the Mg-Zn supernatant phase, which was discarded.

5. Decomposition of Uranium-Zinc Intermetallic Compound by Magnesium

When the intermetallic-compound precipitation step was used, the intermetallic compound was decomposed at 700°C by adding magnesium and forming a Mg-27 at. % Zn alloy from which metallic uranium precipitated. The solution was cooled to 450°C, thereby reducing the uranium solubility to about 0.009 at. %. During this operation, the uranium particles clumped to nearly theoretical density. The Mg-Zn supernatant phase was then discarded.

6. Uranium Product Dissolution

The uranium precipitate is dissolved in a Zn-30 at. % Mg alloy at 810°C to facilitate transfer of the product for the final process step. Although the solubility of uranium in this alloy at 800°C is about 4.0 at. % (18 wt %), the process provides for a uranium concentration of 3.0 at. %.

7. Solvent Evaporation

The Zn-Mg-U product ingot is charged to a beryllia crucible and subjected to a low-pressure retorting operation (650-900°C at ~10 Torr) to remove the magnesium and zinc. The uranium is consolidated into an ingot by heating the crucible to about 1200°C. This uranium ingot is suitable for recycle to the melt-refining operation, and the condensed Mg-Zn vapors are discarded as waste.

B. Flowsheet Development

The original skull-reclamation process flowsheet shown in Fig. 2 required two furnaces, which used two crucibles fabricated of different materials (tungsten and beryllia), and a retort. In this flowsheet, the

Oxidized Skull: 2 kg   Zinc: 35 kg
                         Salt:* 8.8 kg

① Noble-metal Extraction @ 800°C-600 rpm
Cool to 525°C 0 rpm → Waste Zinc: 34 kg (Nobler Fission Products)

Zn-12 at. % Mg: 32 kg → | Zn Salt UO₂ |

② Uranium Oxide Reduction @ 800°C 600 rpm → Waste Salt: 8.8 kg

Zn-Mg-U

③ Uranium-Zinc Intermetallic Precipitation
Cool to 525°C 80 rpm → Waste Zn-10 at. % Mg: 30 kg (Zirconium)

Magnesium: 9 kg | U₂Zn₂₃

④ Intermetallic Decomposition @ 800°C 600 rpm

Zn-Mg-U

⑤ Uranium Precipitation @ 450°C → Waste Mg-27 at. % Zn: 11 kg (Rare Earths)

Uranium Product to Retorting: 2.5 kg

*MgCl₂–47.5 mol % CaCl₂–5 mol % MgF₂.

Fig. 2. Original Flowsheet for Skull-reclamation Process (Steps 1 and 2 performed in tungsten crucible; steps 3, 4, and 5 performed in beryllia crucible)

noble-metal extraction and uranium reduction steps are carried out in a tungsten crucible. The waste salt is separated at 800°C, and the Zn-9 at. % Mg-1 at. % U solution is transferred to a beryllia crucible in the second furnace. The Mg-Zn-U solution is cooled to 525°C to precipitate the U-Zn intermetallic compound (U_2Zn_{23}), after which the Zn-Mg supernatant phase is transferred to waste. The U-Zn intermetallic compound is decomposed at 800°C with the addition of magnesium to produce a Mg-27 at. % Zn solution in which uranium is soluble to only 0.065 at. %. The solution is then cooled to 450°C to precipitate additional uranium (uranium solubility: 0.009 at. %), and the Mg-Zn waste supernatant is transferred from the beryllia crucible. The uranium cake is removed from the beryllia crucible by mechanical means and charged to a retorting furnace for evaporation of the remaining magnesium and zinc.

The original flowsheet was modified because of difficulties encountered in fabricating large beryllia crucibles that are satisfactory for the process operations. These difficulties led to the consideration of performing all process steps in a tungsten crucible. This method of process operation, shown in Fig. 3, has the following advantages:

1.   One furnace is eliminated.

2.   High-temperature separation of the reduction salt from the liquid-metal phase is eliminated.

3.   One transfer tube is eliminated.

The disadvantages of this procedure are:

1.   The uranium product may become contaminated with residual salt.

2. Uranium product is removed as a solution, requiring retorting of larger volumes of magnesium and zinc. This procedure is necessary because of the adherence of uranium to the tungsten crucible

Skull-reclamation process demonstration runs following this flowsheet (Fig. 3) produced good uranium reductions (98-100%), but led to high uranium losses (3-27%) through entrainment during the removal of the Zn-10 at. % Mg supernatant solution. Specially designed strainer weirs were fitted to one end of each transfer tube to reduce uranium entrainment, but these were only moderately successful.

A final modification was made to the flowsheet, as shown in Fig. 4. The intermetallic precipitation and decomposition steps, involving
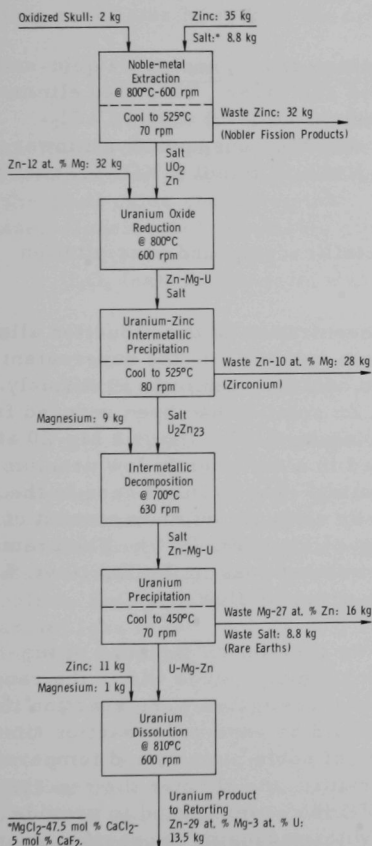

Fig. 3. Modified Flowsheet for Skull-reclamation Process (All steps performed in one tungsten crucible)
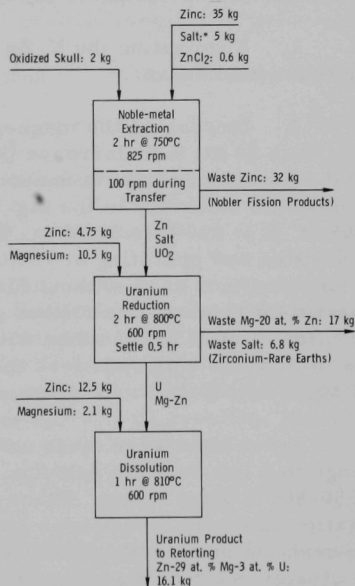
Fig. 4. Final Flowsheet for Skull-reclamation Process

three time-consuming cooling and heating cycles between 800 and 450 or 500°C, were eliminated. Reduction of the uranium oxide is accomplished with a Mg-20 at. % Zn solution, from which the uranium precipitates as a compact cake. After the Mg-20 at. % Zn supernatant metal and waste salt are removed, the precipitated uranium is dissolved in a Zn-30 at. % Mg solution, which is transferred to a retorting vessel to recover the final uranium product.

The advantages of this flowsheet, as compared with the previous ones, include a reduction of material consumption (and consequent reduction of waste volume), as well as an increase in uranium recovery.

The heating and cooling cycles were eliminated in the new flowsheet by:

1. Transferring the waste-zinc phase from beneath a liquid-salt phase rather than from beneath a solidified salt layer. This also eliminated the need for the high-melting salt previously used (47.5 mol % $CaCl_2$-47.5 mol % $MgCl_2$-5.0 mol % CaF_2; m.p., ~600°C); consequently, a lower-melting salt (47 mol % $MgCl_2$-27.7 mol % NaCl-18.6 mol % KCl-6.7 mol % NaF; m.p., ~495°C) could be used.

2. Eliminating the U-Zn intermetallic-compound precipitation step mentioned above.

3. Increasing the magnesium concentration in the reduction alloy from 73 to 80 at. % to decrease the uranium solubility in the supernatant metal solution and make it unnecessary to cool the solution. Previously, the uranium solubility in the Mg-27 at. % Zn solution had been reduced from 0.065 at. % at 800°C to 0.008 at. % by cooling to 450°C. Using a Mg-20 at. % Zn solution and operating at 750°C resulted in a sufficiently low uranium solubility of 0.02 at. % without further cooling. The uranium loss in the supernatant solution was further reduced by using a minimum amount of reduction alloy (33% less than with the Mg-27 at. % Zn alloy). The uranium loss in this waste alloy is less than the combined loss in the Zn-10 at. % Mg and Mg-27 at. % Zn waste solutions of the previous flowsheet.

Seven runs were made using the new flowsheet. Because of the change to a low-melting salt flux, operating temperatures within the range of 650-800°C were tested. Other variables investigated were reaction time, agitation intensity, and charge size. As would be expected, reaction time (for uranium oxide reduction or extraction of noble metals) and temperature are closely related; the higher the temperature, the shorter the reaction time. A reaction temperature of 750-800°C is recommended to provide rapid reactions (complete within 1-2 hr) without causing excessive vaporization of metal- and salt-phase constituents. Good agitation intensity is also necessary to complete the reactions within a short period of time.

In one run, a double charge of uranium oxide and salt was used. In the noble-metal extraction step, the quantity of uranium oxide was so great that when stirring was discontinued to allow the zinc and salt phases to separate, a large amount of the oxide, which normally accumulates at the interface, settled through the zinc phase. An excessive amount of this settled oxide was entrained during the transfer of the waste zinc, causing a high uranium loss.

Since an overall uranium recovery of 99.5% for the processing step of the fuel cycle was desired, the skull-reclamation process was developed to recover at least 93% of the uranium in the melt-refining skulls, which, on the average, contain 7% of the uranium charged. Achievement of a high uranium recovery in the skull-reclamation process requires that the following conditions be met in the noble-metal extraction and reduction steps:

1. Noble-metal Extraction Step

Sufficient oxidizing power must be available to oxidize (1) the uranium and the magnesium metal present in the heel from the product dissolution step of the previous run and (2) any unoxidized uranium metal in the skull oxide charg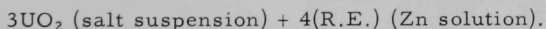e so that all the uranium will transfer to the salt phase. Considerable oxidizing power is available through reactions such as:

$$U_3O_8 \text{ (salt suspension)} + U \text{ (Zn solution)} \rightarrow 4UO_2 \text{ (salt suspension)},$$

and

$$2(R.E.)_2O_3 \text{ (salt suspension)} + 3U \text{ (Zn solution)} \rightarrow$$

$$3UO_2 \text{ (salt suspension)} + 4(R.E.) \text{ (Zn solution)}.$$
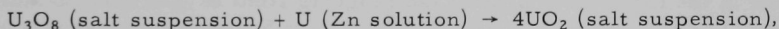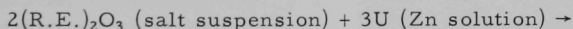
The second reaction is possible because of low activity of rare earths in zinc solutions.[9] Zinc chloride was usually added in the pilot-plant runs. The noble-metal extraction step was performed at 750°C, rather than 800°C, to reduce the $ZnCl_2$ vapor pressure. Since the volatility of $ZnCl_2$ can be a problem, ZnO may be a more convenient reagent. In the pilot-plant runs, uranium loss in the noble-metal extraction step was no problem, generally being well below 0.5%.

2. Reduction Step

To achieve complete reduction and thus avoid excessive uranium losses in the waste salt, the conditions must include sufficient agitation (~600 rpm) and a sufficient reduction time. Uranium losses in the waste salt averaged ~1%. The minimum attainable uranium loss in the salt, which is due to the equilibrium concentration in the salt, is about 0.6%.

Although most of the reduced uranium precipitates from the Mg-20 at. % Zn alloy, a loss of 1.4% occurs as a result of uranium solubility in the supernatant metal solution. Higher losses, which resulted from entrainment were experienced in some runs. The entrainment was not encountered if the precipitate was formed at temperatures above 775°C where the gamma uranium phase exists. This phase is plastic, and the particles agglomerate. In runs in which the precipitate was formed at 700°C, entrainment was minimized (up to 1.0% of the uranium) by allowing a settling period of 0.5 hr before transferring and by transferring the waste-metal and salt phases with stirring at an agitation speed of only 100 rpm. This agitation suspended MgO in the salt while only partially suspending uranium in the metal. An agitator speed of 400 rpm resulted in loss of most of the uranium.

C. Pilot-plant Equipment

The equipment used in the pilot-plant studies included two mild-steel bell jars (24 in. in diameter and 36 in. high) containing tungsten processing crucibles.[10] The tungsten crucibles were heated by induction heating of a 5/8-in.-thick graphite susceptor. The induction coils were cooled by natural convection and radiation to the water-cooled bell-jar wall. This equipment was located inside a glovebox that was 13.3 ft long, 8.5 ft high, and 3.3 ft wide. A dry N_2-Ar atmosphere was maintained in the enclosure and in the furnaces to protect the reagents from oxygen and moisture. Figure 5 shows the glovebox, furnaces, and control panelboard before the glovebox windows were installed. Figure 6 shows a heated transfer line in position for transferring molten metal from one furnace to the other. Although two furnaces were used in the early process flowsheets, only one furnace was used in the final flowsheet, and all transfers were made to a waste or product receiver. Molten materials were transferred by pressurizing one of the furnaces with argon. The bell-jar covers had three ports, one of which was used for an agitator shaft, and the other two for inserting transfer tubes and other equipment used for sampling, liquid-level measurement, and temperature measurement. Figure 7 is a schematic cross-sectional view of the furnace with the transfer line.

108-5968

Fig. 5. Pilot-plant Glovebox and Control Panels
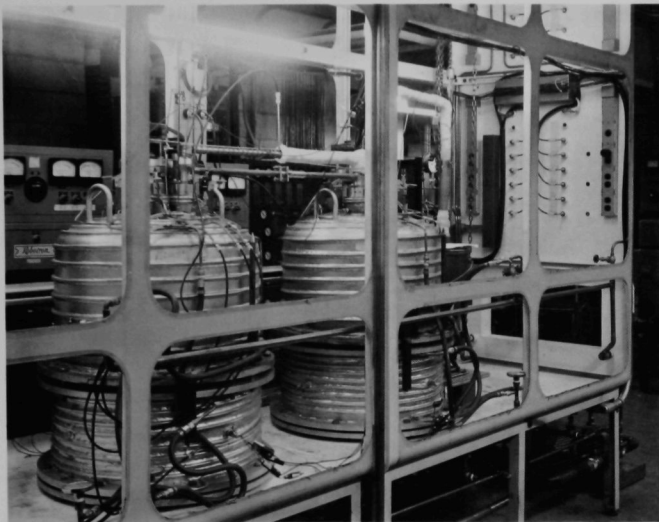
108-5970

Fig. 6. Bell-jar Induction Furnaces
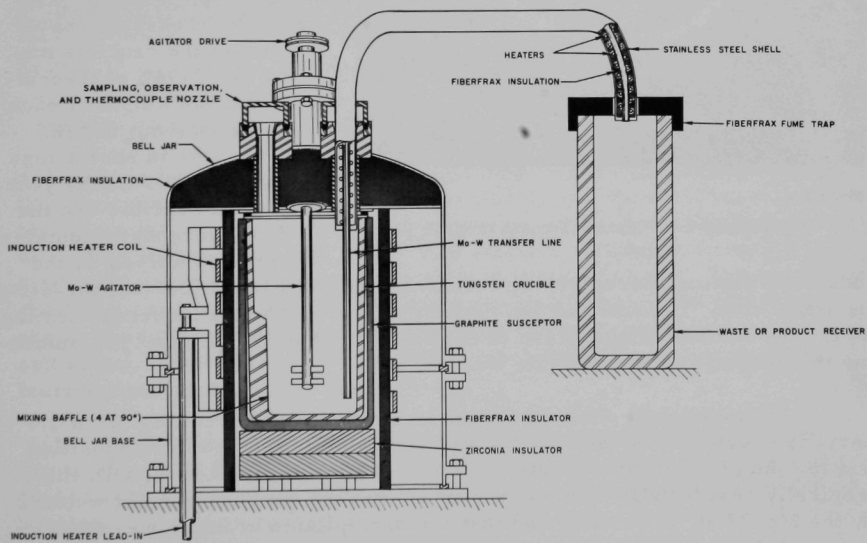
108-7134 Rev. 1

Fig. 7. Bell-jar Furnace for Skull-reclamation Process

16

The bell jar and the service nozzles in the top were water-cooled to prevent damage to rubber gaskets. When the crucibles were at 800°C, the temperature of the rubber gaskets was 40°C, a temperature that is well below the permissible operating temperature of the gaskets (150°C). During the runs, a continuous argon gas purge (5 cfh) was introduced into the three bell-jar nozzles to inhibit the accumulation of condensed metals and salt around the agitator shaft, the sample port, and the transfer tube.

Tungsten crucibles were used to contain the molten salts and metals. Figure 8 shows a pressed-and-sintered tungsten crucible (12 in. in OD and 20 in. high) with integral mixing baffles. This is one of three such crucibles fabricated by Union Carbide Nuclear Corporation, Oak Ridge, Tennessee. The density of the crucible material is 92-94% of theoretical, and the weight of each c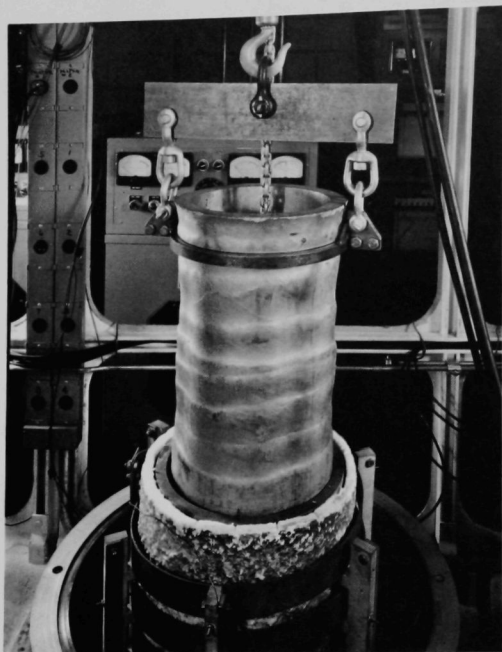rucible is about 500 lb. The crucible is shown suspended from its lifting yoke. Below the crucible are the graphite secondary container (which also serves as the induction-heating susceptor), an insulating sleeve, and the flat-copper-strip induction coil. The coil was powered by a 30-kW, 10-kHz induction-heating unit. The surface temperature of the coil was about 300°C when the operating temperature of the crucible was 900°C.

108-5962

Fig. 8. Pressed-and-Sintered Tungsten Crucible

In the original skull-reclamation process flowsheet (Fig. 2), a beryllia crucible was used for the U_2Zn_{23} precipitation and decomposition and for the uranium precipitation. Small-scale studies in 4-in.-OD, thixotropically cast beryllia crucibles showed that the beryllia was not wetted by the Mg-27 at. % Zn alloy and that the precipitated uranium was easily removed from the crucible. However, three 12-in.-OD, 20-in.-high thixotropically cast crucibles (Fig. 9) that were exposed to Zn-9 at. % Mg-1 at. % U, Mg-27 at. % Zn plus precipitated uranium, and

Zn-29 at. % Mg-3 at. % U at 810°C developed circumferential cracks, which allowed metal to leak from the crucibles. The integrity of large thixotropically cast crucibles was too poor for process use.

108-7649

Fig. 9

Thixotropically Cast Beryllia Crucible

In the initial flowsheet, the melt was cooled in the noble-metal extraction step and the two uranium precipitation steps. This was accomplished by circulating the argon gas from within the bell-jar furnace through a closed heat-exchanger system located below the glovebox (as shown in Fig. 10). A Model 297-6 Leiman pump was used to circulate the argon gas through the bell-jar furnace and a water-cooled Brown Fintube heat exchanger during the melt-cooling operations. A heat-transfer study was made during one run (Run SKR-20) to determine the heat removed by the cooling coils located on the bell-jar furnace and by the heat exchanger that cooled the circulating argon gas. The results showed that an average of 35% of the heat (2.2 kW) was removed by the heat exchanger and that 65% of the heat was removed (4.06 kW) by the cooling water on the bell-jar furnace wall and base.

An alloy of Mo-30 wt % W was used for components that required machining and were to be exposed to process solutions. These components included the mixer shaft and blades, small heat shields for the shaft bearing assembly, and a large heat shield, which covered the crucible. The agitator blades were 4.25 in. long and 1 in. wide. The original agitator shaft was a 0.5-in.-diam rod, but it was replaced by a 0.75-in. hexagonal bar. The hexagonal shaft was used to provide the required gas path through the frozen-salt phase when molten metals were to be transferred from below a solidified-salt phase. Slow rotation of the hexagonal agitator shaft during the salt-freezing period maintained the opening.

Figure 11 shows the complete agitator and support assembly. Three Mo-30 wt % W heat shields are located just below the Graphitar guide bearing to prevent salt and metal vapors from depositing in the bearing.

Heat shields (12-in. OD, 0.1 in. thick) fabricated of Mo-30 wt % W were positioned on the top of the tungsten crucible. (Pure tungsten heat shields often crack and delaminate.) The Mo-30 wt % W heat shields were

unaffected by heat or corrosion. An additional heat shield fabricated from Hastelloy-X was located in the upper portion of the furnace bell jar. Heat shields fabricated from Type 304 stainless steel warped in this application.
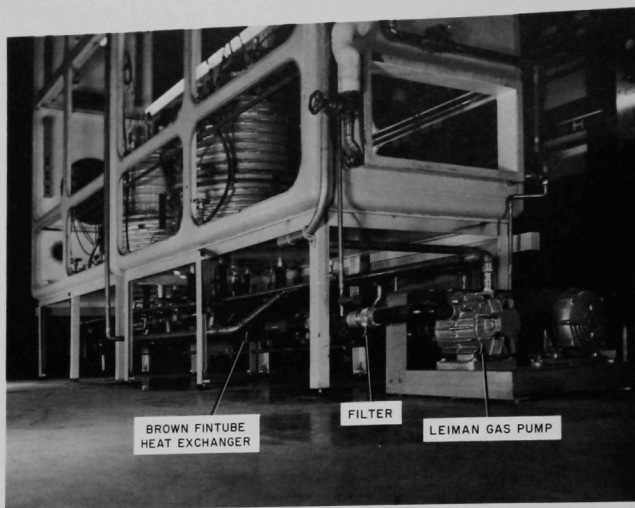
108-5973A

Fig. 10. Furnace-gas Cooling System
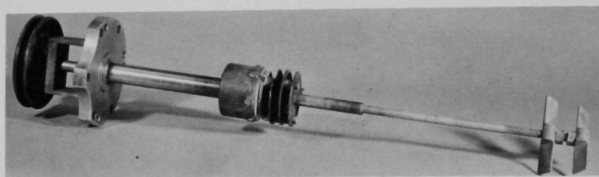
108-6818

Fig. 11. Agitator, Heat Shields, and Support Assembly

Waste and product streams were removed from the tungsten process crucible through Mo-30 wt % W heated transfer tubes formed in the shape of an inverted J.[11] The first transfer tubes used were fabricated from 5/8-in.-OD, 5/16-in.-ID, gun-drilled Mo-30 wt % W alloy rod, which was assembled by means of threaded elbows. Continuous transfer-tube development resulted in an improved design consisting of two lengths of gun-drilled rod (3/4-in. OD, 3/8-in. ID) coupled together to form a single 78-in.-long tube. The bends were made by hot-forming instead of using threaded elbows.

The transfer tubes were heated to 800°C with a number of 600-W heating cables, which were wound on the tube. The cables were magnesia insulated and had a 1/8-in.-OD stainless steel sheath. The heaters were covered with insulation and then enclosed with a stainless steel envelope. The envelope protected the insulation and heaters during handling, and the annular space between the envelope and the tube could be evacuated and filled with argon to prevent oxidation of the Mo-30 wt % W tube. Figure 12 shows a typical transfer tube.

VACUUM AND PRESSURE TAP FOR ENVELOPE

THERMOCOUPLES

ELECTRIC HEATER LEADS

FURNACE SEAL

Mo-30 wt% W PROTECTIVE CAP
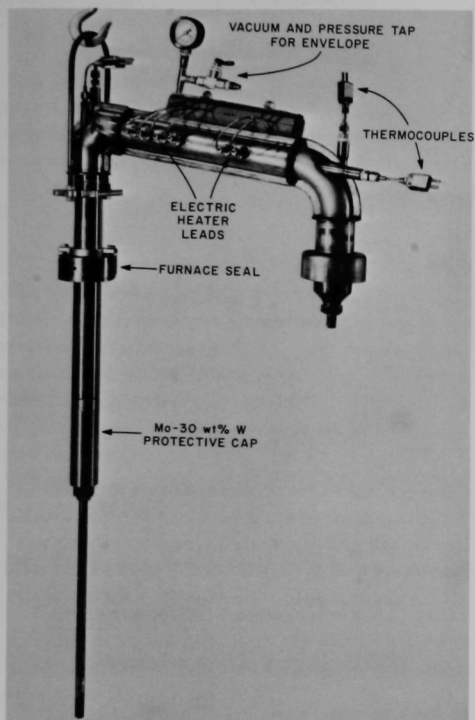
108-7357A

Fig. 12. Heated Mo-30 wt % W Transfer Tube

The material discharged from the process crucibles through the transfer tubes was collected in a graphite mold suspended from a spring scale. Close observation of the scale permitted control of the quantity of material removed in any transfer.

One hand-operated and three electrically operated chain hoists were used for lifting and moving process components within the glovebox.

The final step in the skull-reclamation process is the recovery of the uranium from the Zn-29 at. % Mg-3 at. % U ingot by distillation of the Zn-Mg.[12] This operation was carried out in the retort assembly (combination still pot, condenser, and collector) shown in Fig. 13. The assembly was located inside a bell-jar furnace to permit operation under low pressure (~10 Torr). A 10-kHz induction heater with about a 7.5-kW power output was used to heat the still pot. A thixotropically cast beryllia crucible with hemispherical interior bottom was used to contain the metal solution during the retorting operation. A graphite secondary container used to support the beryllia crucible also acted as an induction-heating susceptor.

Proper performance of the retorting equipment requires close control of the power input to avoid surging or bumping. The furnace was equipped with a seismic-vibration detector and a contact microphone to warn of the approach of excessive boilup.
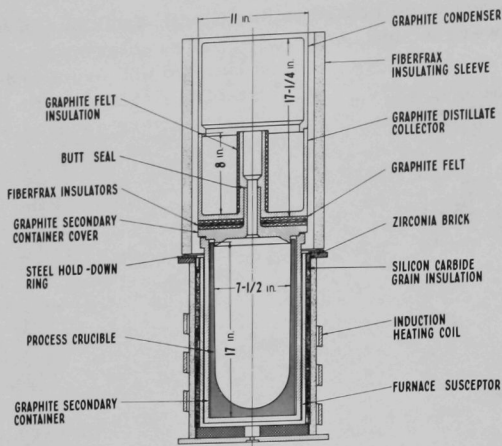
Fig. 13

Retort Assembly

108-8736

III. PILOT-PLANT OPERATING EXPERIENCE

A total of 36 skull-reclamation process demonstration runs were made to test the equipment and to develop processing techniques that would provide sufficient fission-product removal and good uranium-product recovery. The scale of operations in these runs was about 2 kg of skull oxide (about 75% uranium). The planned full-plant scale was about 7 kg of skull oxide (5 kg of uranium).

A. Mechanical Performance

The mechanical performance of the equipment was generally satisfactory. The pressed-and-sintered tungsten crucible and the Mo-30 wt % W agitator shaft and impeller showed excellent corrosion resistance.

The final design of the heated transfer tube gave excellent service and, with the proper techniques, allowed for close control of solution transfer operations. The transfer line was fixed in the furnace with its inlet point about 1/2 in. above the crucible bottom. All transfers were made by pressurizing the furnace with argon. When only the metal phase was to be transferred (e.g., the zinc phase following the noble-metal-extraction step), the furnace was pressurized until the desired amount of metal had been removed as indicated by the weight of the receiver. The gas pressure was then vented through a relief valve, and the transfer was abruptly stopped. These transfers were controlled at 90% removal of the metal to avoid inadvertent transfer of the molten salt in which skull oxide was suspended. When relatively complete transfers were desired (e.g., transfer of salt and magnesium-zinc after the reduction step), the furnace was pressurized

until excess argon pressure vented through the empty transfer line. With this technique, approximately 95% of the available molten material was transferred from the furnace.

Phase transfer efficiencies of about 90% were realized in transferring the product solution. Product solutions are small in total volume compared with the waste solutions, and lower transfer efficiencies were expected. The portion of the product solution that was not transferred was recycled through the next run.

B. Salt Foaming

A salt-foaming problem attributable to water of hydration in the salt developed during the reduction step of several early process-demonstration runs. Several methods of salt pretreatment, such as vacuum melting and contacting the molten salt with magnesium to remove the water, were tried as alternates to the proven technique of bubbling hydrogen chloride through the molten salt. The magnesium pretreatment was used in preparing salt for runs subsequent to SKR-20. This is a simple foundry-type operation in which magnesium and any water in the salt react to form hydrogen and magnesium oxide at 700°C. In these runs, the small amount of magnesium oxide formed in the salt was not objectionable and filtration was not necessary. The dry inert atmosphere in the processing glovebox prevented absorption of water during subsequent experimental operations.

C. Fission-product Removal

Table I lists fission-product removals for a number of the skull-reclamation process runs.

In the noble-metal-extraction step, ruthenium and molybdenum are relatively insoluble in zinc at the phase-transfer temperature of 525°C. Therefore, the zinc phase was agitated at 400 rpm during the transfer to keep the molybdenum and ruthenium that were extracted from the salt phase in suspension in Runs SKR-12 through SKR-28. In Runs SKR-29 to -36, the molybdenum and ruthenium were in suspension when the waste zinc was transferred at 700°C with a mixing speed of only 100 rpm.

Ruthenium removals were satisfactory and ranged from 58 to 97%, but the removal of molybdenum varied between 14 and 71% in these runs. Extraction time, temperature, and mixing speed appeared to have little effect on molybdenum removal. Since the solubility of molybdenum is very low in the product solution, an unsuccessful attempt was made to enhance the molybdenum removal in Runs SKR-31 and -32 by allowing a 15- to 30-min settling period before transfer of the product solution. Unfiltered samples of the product solution before the transfers showed a low

concentration of molybdenum, but subsequent analyses of the transferred product solution showed that it contained about 45% of the molybdenum originally charged.

TABLE I. Fission-product Material Balances in Skull-reclamation Process Runs

	Percentage of Fission Product Charged														
	Noble-metal Extract		Supernatant Inter-metallic Precipitation		Supernatant Inter-metallic Decomposition	Waste Flux		Product Solution[a]				Total Percentage of Fission Product Accounted for			
Run No.	Mo	Ru	Ce	Zr	Ce	Ce	Zr	Mo	Ru	Ce	Zr	Mo	Ru	Ce	Zr
SKR-9	25	79	3	42	39	30	-	55	17	8	41	75	96	80	83
SKR-10	58	92	0.6	60	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SKR-11	42	73	4	62	38	6	11	15	20	25	28	57	93	73	101
SKR-12	71	97	12	70	21	5	2	23	12	37	28	94	109	75	100
SKR-13	60	89	4	53	38	35	5	39	21	5	36	99	110	82	94
SKR-14	45	75	NA	45	23	45	NA	41	16	6	34	86	91	74	79
SKR-15	57	82	NA	42	32	37	NA	44	14	13	50	101	96	82	92
SKR-16	61	74	NA	47	36	31	NA	28	17	5	30	89	91	72	77
SKR-17	60	84	NA	54	39	29	6	17	9	5	19	77	89	87	69
SKR-19	57	75	NA	45	37	16	45	15	7	6	23	72	82	59	113
SKR-20	38	67	NA	24	24	37	24	27	24	5	52	65	91	66	100
SKR-21	45	65	NA	42	41	9	42	26	19	15	30	71	84	65	114
SKR-24	14	58	NA	40	45	42	40	50	21	5	37	64	79	92	119
SKR-25	44	75	NA	44	33	44	44	39	6	7	27	83	81	84	115
SKR-27	42	67	NA	15	69	2	31	30	10	7	36	72	77	78	82
SKR-28	51	73	NA	28	60	1	29	26	16	13	30	77	73	74	87
SKR-33	47	77	40	NA	NA	30	NA	20	13	10	NA	67	93	46	NA
			60 wt % Mg-Zn Supernatant												
			Ce	Zr											
SKR-29	33	75	36	31		37	8	47	13	7	51	80	88	75	90
SKR-30	35	85	36	32		39	25	51	37	5	50	86	122	76	107
SKR-31	19	82	29	41		43	6	11	13	7	37	30	95	91	84
SKR-32	22	79	27	30		41	13	6	16	7	35	28	95	78	71

[a]Before transfer.
NA: No Analysis.

Zirconium removal in the supernatant Zn-12 at. % Mg after the reduction and intermetallic precipitation step varied between 15 and 70%. The zirconium removal in the waste salt varied between 2 and 45% and depended on the extent of reduction of ZrO_2 by the Zn-12 at. % Mg solutions. In the final flowsheet (Fig. 4), where the intermetallic precipitation and decomposition steps are eliminated, reduction in the Mg-20 at. % Zn solution resulted in zirconium removals of 50-65% based on product-solution analyses. Zirconium was removed in the waste salt as unreduced ZrO_2 and in the supernatant Mg-Zn as a result of a slight solubility in the solution.

Cerium is removed in the magnesium-rich supernatant solution and in the waste salt. Cerium, a stand-in for all rare-earth elements, showed an overall removal of greater than 90% based on product-solution analyses.

D. Uranium Losses

Uranium losses in the noble-metal extraction step of all skull-reclamation process runs averaged about 0.4%. Transfer of the supernatant Mg-20 at. % Zn at 700°C after reduction at 800°C resulted in uranium losses of about 1.4%.

Losses of uranium in the waste salt reflect the reduction efficiency and varied between 0.3 and 1%. Chemical analyses show that the uranium present in the product solutions averaged about 95% of that charged.

E. Retorted Products

Several Zn-29 at. % Mg-3 at. % U product ingots were retorted in the pilot-plant retorting unit (Fig. 13) to remove the Mg-Zn alloy and to recover the uranium in ingot form. The Mg-Zn distillate was satisfactorily contained within the graphite retorting enclosure by careful control of the vaporization rate using the seismic-vibration detector and contact microphone.

Beryllia was the only crucible material found that would contain the molten Zn-Mg-U alloy and yet would release the final uranium ingot. Thixotropically cast beryllia crucibles manufactured by the Brush Beryllium Company of Elmore, Ohio, were used in the retorting step. The beryllia crucibles performed satisfactorily, but after each run about 25 g of uranium was found in the annulus between the beryllia crucible and the graphite secondary container. The loss of uranium was attributed to seepage of the Zn-Mg-U solution through the crucible wall. Efforts by the manufacturer to reduce the seepage resulted in crucibles having less resistance to thermal shock. Since the crucibles were expensive, the very small seepage of uranium was considered to be acceptable. The uranium in the secondary crucible can be recycled.

Analyses of several retorted products are given in Table II. Analyses of the distillates from these runs have shown uranium entrainment to

TABLE II. Analyses of Retorted Uranium Product Ingots

| | | | Recovered Product Ingot | | | | | | | |
| | Total Charge (from U Dissolution Step), kg | Distillate Mg-Zn, kg | U, kg | Percentage of Fission Product Removed | | | | Mg, ppm | Be, ppm | Zn, % |
Run No.				Ce	Zr	Mo	Ru			
SKR-13	11.29	9.95	1.05	97	68	67	75	-	20	-
SKR-15	12.92	11.30	1.25	96	60	62	85	400	5	<1
SKR-16	13.14	11.50	1.17	98	74	71	85	8	25	-
SKR-23	12.61	11.36	1.15	97	62	56	64	700	100	0.4
SKR-29	15.90	14.28	1.48	95	43	62	47	400	400	0.2
SKR-30	12.67	11.40	1.22	89	68	78	88	300	400	0.08

be negligible (0.01%). Magnesium and zinc contamination of the product uranium was low (~500 ppm). Beryllium and carbon contamination of the product resulting from the use of beryllia crucibles and graphite condensers was not significant. Carbon analyses indicated about 0.01% carbon, which is well below the maximum specified for reactor-grade uranium. Fission-product concentrations were satisfactorily low, and the product was suitable for return to the main EBR-II fuel stream via the melting-refining operation.

IV. CONCLUSIONS

The skull-reclamation process flowsheet was established during the pilot-plant investigations, and process procedures and techniques were developed. All steps of the process were successfully demonstrated.

The overall mechanical performance of the equipment was good and demonstrated that the equipment could be adapted to the remote operation required in a processing plant. Tungsten, Mo-W alloy, and beryllia proved to be suitable materials of construction for process equipment that is required to withstand the temperature (~800°C) and corrosive effects of the molten salts and metals in the process. Although fabrication of large tungsten and beryllia crucibles was difficult and expensive, these items were fabricated and gave satisfactory service. The heated transfer lines fabricated from gun-drilled Mo-W alloy gave very good service with both liquid metals and molten salts.

With the successful completion of the pilot-plant studies of the skull-reclamation process, the fabrication and testing of prototype equipment for use with EBR-II fuel were initiated.[13] The equipment and techniques used in the skull-reclamation process are also adaptable to other pyrochemical processes. Some of these techniques have also been used at Argonne in the plutonium salt-transport process for oxide fuels.[14]

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